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Effect of temperature on thermochemical property and true density of torrefied coffee residue

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ABSTRACT

Torrefaction is a mild pyrolysis process in the relatively low temperature, which aims to upgrade the thermochemical and physical properties of biomass as a high energy-density fuel. In this study, coffee residue, a processing by-product from the soluble coffee industry, was torrefied at the temperature range of 503–623 K with residence time of 10 min by a commercial electric oven. The thermochemical properties of the torrefied biomass, such as elemental analysis and calorific value, were investigated. Furthermore, the information about microscopic and structural characteristics was also obtained by means of scanning electron microscopy (SEM) and true density. It was found that the calorific value of the torrefied biomass increased with temperature, while its maximal increase occurred at around 563 K. This result was in high agreement with the observation from the thermogravimetric analysis (TGA) of coffee residue. More consistently, the carbon content of torrefied coffee residue increased significantly as temperature increased from 563 to 593 K, which should be the temperature window of torrefaction for this biomass. By contrast, the contents of hydrogen and oxygen decreased slightly due to the devolatilization as a result of thermal decomposition reactions like dehydration and depolymerization. On the other hand, the true density of torrefied coffee residue increased with temperature at above 563 K, making it more observable in the structural shrinkage as also depicted in the SEM. However, it may involve light gases released and loose structure remained at temperature of below 563 K, leading to decreased true density with temperature from 503 to 563 K.

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1. Introduction

The reuse of renewable bioresources as alternative fuels in replacement of fossil-based fuels has received much attention in recent years. This transition from non-renewables to renewables is mainly due to the environmental issues, including acid rain, air toxics and global warming. The energy supply from domestic biomass resources not only enhances fuel diversification, but also reduces the air pollution because the biomass resource contains relatively low contents of sulfur and heavy metals in comparison with fossil fuels such as coal [1]. In this respect, agricultural residues contain large amounts of lignocellulosic constituents (i.e., cellulose, hemicellulose and lignin) and thus possess high-energy contents [2,3]. Therefore, they can enrich available carbon sources in the production of biomass energy based on benefits of both energy utilization and environmental protection.

Coffee is one of the most important agricultural commodities in the world because it is a popular brewed drink prepared from roasted bean in the food processing industry. Inevitably, coffee residue will originate from soluble or instant coffee production during the extraction process. The residue weighs approximately 50% of the total input mass of coffee feedstock, representing a significant bioresource from the coffee-derived products. In Taiwan, for example, the estimated quantity of exhausted coffee residue was approximately 10 thousand metric tons based on about 20 thousand metric tons of imported coffee (not roasted and not decaffeinated) in 2011. Because of its high organic contents such as carbohydrate, protein, fiber, caffeine, polyphenols, tannins, and pectins, this bioresource was traditionally suitable as an animal feed, soil conditioner, and organic fertilizer [4]. In addition, it can be further reused as a potential feedstock to produce useful products such as enzymes, organic acids, flavors and aroma compounds from the extractives [5], and anti-pest agents from the pyrolysis bio-oil [6]. On the other hand, this dried biomass characterizes its high content of carbon source, suggesting that it can be directly reused as a biomass fuel in mills [2,3].

However, the use of raw biomass residue as a fuel often faces several problems, including large bulk volume, high moisture content, low heating value and energy density, hygroscopic nature, and smoke during combustion, making it low in combustion efficiency

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[7]. In order to overcome some of the aforementioned limitations of biomass material, thermochemical conversion is a promising route to convert lignocellulosic biomass to fuel and renewable materials [8,9]. Among these thermal methods, pyrolysis is a thermal decomposition of the biomass in an inert atmosphere at mediate temperature into biochar (carbon-rich material) and other pyrolytic products. Recently, torrefaction, a mild pyrolysis, is currently being considered for improving the thermochemical properties of biomass, and also producing a hydrophobic solid product with an increased energy density [10–13]. In this process, biomass is generally heated from 473 to 623 K in the absence of oxygen. Torrefied biomass products have been proposed as available feedstocks for direct combustion, gasification and coal co-combustion due to its high energy content, good grindability, and hydrophobic properties [10].

In view of reusing coffee residue as a precursor for the production of torrefied biomass, few research works studied on this [14,15]. Chen et al. [14] employed a simple tube furnace to conduct torrefaction experiments for coffee residue at 513 and 543 K with residence times of 0.5 and 1.0 h. They concluded that coffee residue is the most active biomass to torrefaction due to its relatively high hemicellulose content. In the study by Dhungana et al. [15], coffee husk was heated at a rate of 20 K/min to 523–553 K with residence times (15–60 min) in a muffle furnace, showing an increase in energy density after torrefaction. In addition, the effects of temperature and residence time on properties of torrefied products were positively observed at the consistent variation. In the previous study [16], the pyrolysis treatment of coffee residue was performed at the temperature of 673–973 K with the heating rate of about 10 K/min in a vertically fixed-bed reactor, yielding a series of biochar products with high calorific value (>30.1 MJ/kg). Furthermore, the resulting biochars were characterized using helium-based solid density (true density), showing that the density increased with increasing pyrolysis temperature. In this work, a series of torrefied products derived from coffee residue were prepared at the lower temperatures (i.e., 503–623 K) with residence time of 10 min in a commercial electric oven. On the other hand, the thermochemical and physical properties of the torrefied biomass by means of calorific value, ultimate analysis, true density and scanning electron microscopy (SEM) were analyzed to observe their variations with torrefaction temperature.

2. Materials and methods

2.1. Materials

The coffee residue was obtained from a local soluble coffee factory in southern Taiwan. This biomass sample with average particle size of about 0.5 mm was first closely stored in a grass bottle. Prior to the thermogravimetric analysis (TGA) and torrefaction experiments, the sample was dried at about 373 K for at least 24 h. According to the previous results on the biomass precursor [16], its thermochemical properties were given below:

- Approximate analysis: moisture 11.5%, volatile 79.5%, ash 0.7%, fixed carbon 8.3%.
- Ultimate analysis: carbon 52.5%, hydrogen 7.0%, oxygen 34.8%, nitrogen 3.5%, sulfur 0.1%.
- Chemical composition: holocellulose 47.2%, lignin 39.4%.
- Calorific value (higher heating value, HHV): 23.5 MJ/kg.

2.2. Thermogravimetric analysis of exhausted coffee residue

In this work, the thermogravimetric analysis of coffee residue sample was carried out in a thermal analyzer (Model: PT-1600; Linseis Co., Germany) under dynamic atmosphere of flowing a high quality nitrogen (99.999% purity). The sample (about 10–15 mg) was spread uniformly at the bottom of the cylindrical crucible made of alumina (Al_2O_3) and then heated with a constant heating rate of 10 K/min from ambient temperature (about 300 K) to 1273 K. During the experiment, the nitrogen gas was used as a purge gas. In this way, the continuous records of sample weight loss and temperature were obtained under an inert atmosphere. From the measured weight loss-versus-time graph, it can provide the information on decomposition reaction mechanism, thermal stability, and so on.

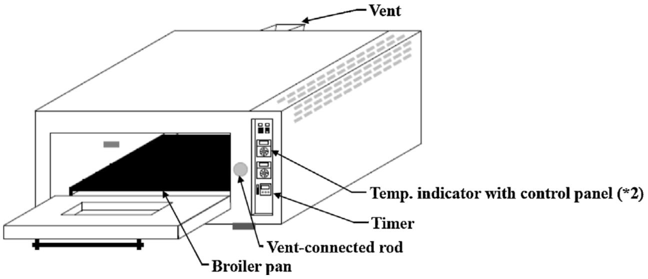


Fig. 1. Schematic diagram of commercial electric oven used as a torrefier.

2.3. Torrefaction experiments

Although several operating parameters (e.g., type of biomass, temperature, residence time, and heating rate) during the mild pyrolysis (or torrefaction) experiments contribute to the characterization of resulting products, the process temperature is expected to be the most important factor because the thermochemical changes are all temperature dependent [17]. Based on the results by Dhungana et al. [15], temperature has a greater effect on torrefaction than residence time has. Thus, the temperature parameter was only considered in the present study. The torrefied products were prepared from the torrefaction of the biomass sample in a commercial electric oven (Model: SC-S64; Max. operation temperature: 673 K; Sheng Shang Industrial Co., Taiwan) as depicted in Fig. 1. The experimental oven made of stainless steel has the inner dimensions of 64 cm (*W*) × 44 cm (*D*) × 20 cm (*H*). There are two K-type thermocouples, which are equipped with the inner wall of the oven at the right side. The biomass sample (about 5 g) was poured into a ceramic crucible with fitting cover to provide a near oxygen-free atmosphere during the torrefaction experiment. The torrefaction temperature was set at 503, 533, 563, 593 and 623 K, respectively. For performing the torrefaction experiments in an efficient manner, the electric oven was first risen up to the prescribed temperature by a power system with two proportional integral derivative (PID) temperature controllers. Then, the crucible containing the biomass, which was promptly placed into the center of the oven, was heated at the prescribed temperature for 10 min to trigger the moisture removal and torrefaction reaction happened. In order to weigh the mass of torrefied biomass, the resulting product was taken from holding crucible and then into the desiccator for cooling to room temperature. The yields (burn-off levels) of the torrefied products prepared in duplicate were thus calculated based on the difference between the masses before and after torrefaction. In order to evaluate the availability of torrefied products as solid fuels, their elemental analyses, calorific values and true densities were further measured as described below.

2.4. Thermochemical property analysis of torrefied product

2.4.1. Calorific value analysis

The higher heating value (HHV), also called gross calorific value, is defined as the amount of heat released by the unit mass of sample. In this work, it was measured in an adiabatic oxygen bomb calorimeter (Model: CALORIMETER ASSY 6200; Parr Instrument Co., USA). In the experiments, about 0.5 g of the torrefied product was conducted in the calorimeter to measure the constant volume heat released by the combustion of the biomass with pure oxygen.

2.4.2. Elemental analysis

The elemental analysis determines the weight fractions of non-mineral major elements (i.e., carbon, hydrogen, nitrogen, oxygen, and sulfur) of torrefied biomass, which can be used to determine its calorific value. The elemental analysis of the torrefied sample (2–3 mg) was conducted by using an elemental analyzer (Model: vario EL III; Elementar Co., Germany) with accuracy of 0.1% and precision of 0.2%. For each analysis, the standard samples (i.e., sulfanilic acid and benzoic acid) were first analyzed for checking the experimental error within ±0.1%.

2.4.3. True density

The true density (sometimes called helium-based solid density and skeletal density) is defined as the ratio of the sample mass to the volume (excluding any pores within the sample) occupied by that mass [18]. In the present work, the cell walls should constitute the major solid content of a torrefied biomass, suggesting that a torrefaction process can reduce the anisotropic behavior and therefore change the permeability of a torrefied biomass [9]. In this regard, helium is the most used probe gas because it can penetrate even the very small pores in the powder biomass sample because of its extreme inertness (avoid being adsorbed) and very small molecule size (about 0.2 nm). A helium displacement method with a pycnometer (Micromeritics Co., U.S.A.; Model No.: AccuPyc 1340) was used to measure the true density of the torrefied sample in this work. Although the measurement of true density of partially pyrolytic (torrefied) biomass is as difficult as the measurement of its true solid volume, this physical property can be used to elucidate its thermal decomposition mechanism during the pyrolysis [9,16].

2.4.4. Scanning electron microscope observation

In order to observe the porous and corrugated texture of torrefied biomass for characterizing structural change on cell wall, this work was examined by using scanning electron microscopy (SEM). The SEM analysis was carried out on the instrument (Model No.: S-3000N, Hitachi Co., Japan) operated at a 15 kV accelerating potential. Prior to the observation, the surface of the sample was coated with a thin, electric conductive gold film.

3. Results and discussion

3.1. Thermogravimetric characteristics of exhausted coffee residue

Thermogravimetric (TG) data (mass loss or percent residual mass versus temperature graph) of coffee residue from the TGA experiment generally reflect the thermal behavior and chemical composition (described in Section 2.1) of the initial sample, intermediate species and final residue, which can used to evaluate the pyrolysis characteristics. In this work, the TG curve of the coffee residue sample in the nitrogen atmosphere at a heating rate of 10 K/min was shown in Fig. 2. It was clearly seen that the thermal decomposition of the biomass seemed to be a gradual process with different regions in the TG curve. The first one ranging from 300 to 500 K represents the stage of moisture dried and loose constituents released (about 5%). When the torrefaction temperature widely ranged from 500 to 670 K (i.e., the second stage), a significant drop in weight was observed. In this stage, the weight of the tested biomass has been reduced to below 40%, where most of the volatiles (about 60 wt%) are released. Furthermore, the torrefaction has a significant impact upon the lignocellulosic structure within the temperature range, implying that the hemicellulose and cellulose components often undergo the greatest amounts of degradation within the temperature ranges of 500–573 and 573–670 K, respectively. The former stage involves hemicellulose depolymerization, leading to an altered and rearranged polysugar structure [9]. The final stage is 670–900 K, where slight mass loss (about 10 wt%) caused by most of the organic residues (e.g., lignin) decomposition reactions was observed. Chen et al. [14] reported similar TGA results for coffee residue.

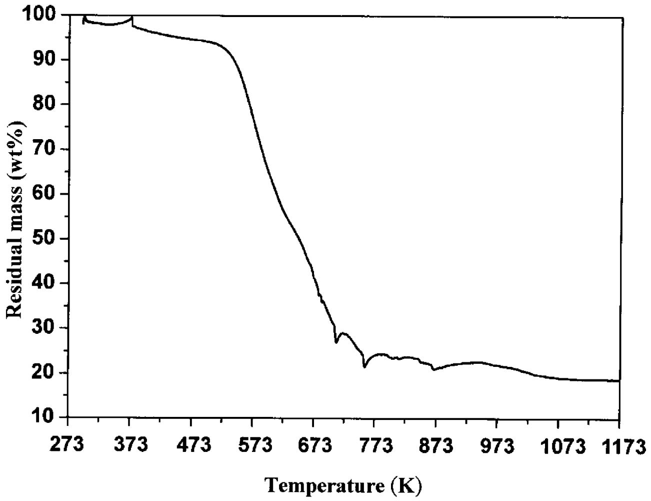


Fig. 2. TGA curve of coffee residue at heating rate of 10 K/min.

3.2. Yields of torrefied products

As described in the TGA, the thermal decomposition of biomass under the torrefaction (or mild pyrolysis) mainly produces three products: solid char product which retains most of the energy content of the feedstock, condensable liquid comprising of moisture, carboxylic acids and other oxygenates, and non-condensable gases such as CO and CO_2 [9]. The last two products can be represented by volatiles. Generally, the total yield of volatiles increases with raising temperature. This result is attributable to the competition between charring and devolatilization reactions, initially occurring in an inert atmosphere at about 570 K [17].

In view of the aforementioned, the experimental torrefaction conditions in the present study were performed at the prescribed temperature (503–623 K). The yields of the torrefied products are in the range of 58.2–98.7 wt%, as shown in Fig. 3. The maximal variation of yield occurred at about 563 K, which should be attributed to the depolymerization of hemicellulose, leading to partial carbonization and volatilization of tar products derived from the lignocellulosic components of coffee residue.

3.3. Thermochemical properties of torrefied products

From the standpoint of energy use of torrefied biomass in replacement of coal, its calorific value is the most important thermochemical property. In Fig. 4, it can be seen that the calorific value of torrefied coffee residue (e.g., around 29 MJ/kg for TCR-623) was relatively comparable to that (i.e., 28.0–32.0 MJ/kg) of fossil coal [19]. As seen in Fig. 4, a maximal increase in the slope of a HHV-Temperature curve (or the rate of change) obviously occurred at about 563 K. In this regard, the value of HHV for the torrefied biomass gradually increased after the temperature of 563 K, and finally reached to a mature condition. In my previous study [16],

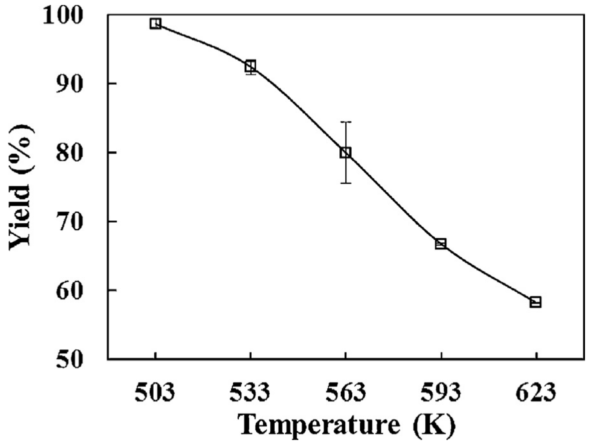


Fig. 3. Yield of torrefied biomass as a function of process temperature.

the pyrolysis temperature of 673 K was found to be optimal for the higher calorific value. This finding was in agreement with the results in the TGA data (Fig. 2) because a significant drop in weight was observed at the torrefaction temperature of ranging from 500 to 670 K (i.e., the second stage). As compared to that of the coffee residue (23.5 MJ/kg, described in Section 2.1), the calorific value of the torrefied biomass (i.e., TCR-623) increased 24%. The experimental results have demonstrated that the torrefied coffee residue may be considered as a charcoal. As a result, torrefied biomass has been proposed as an available feedstock for gasification due to its high energy content, good grindability, and hydrophobic properties. In the gasification process, biomass can be gasified at lower temperatures than coal because its main constituents, the high-oxygen cellulosics and hemicellulosics, have higher reactivities than the oxygen-deficient, carbonaceous materials in coal. However, the biomass-gasification processes are complex and require large investments to prevent damage to downstream equipments and poisoning of downstream catalysts [20]. For example, tar formation is one of the major problems to deal with during biomass gasification because it condenses at reduced temperature, thus blocking and fouling process equipments such as engines and turbines.

It is well known that the thermochemical property of solid fuel can be related with its elemental analysis. Given in Table 1 were the results of the elemental analysis of these torrefied products (i.e., TCR-503, TCR-533, TCR-563, TCR-593, and TCR-623). The torrefied biomass (i.e., TCR-623) contained about 67 wt% of carbon, which is obviously higher than that (i.e., 52.5 wt%) of the raw precursor as described in Section 2.1. More significantly, the carbon content of torrefied biomass increased mostly within the temperature range (563–593 K), which should be the temperature window of torrefaction for coffee residue. This result was consistent with the abovementioned discussion on the variations of the yield and calorific value. Furthermore, the torrefied products contained high concentrations of O and H, but the data significantly decreased with increasing temperature. For instance, the contents of O and H were reduced from 32.53 and 6.00 wt%, respectively at 563 K to 24.73 and 5.46 wt% at 593 K. As a result, both the molar ratios of O/C and H/C of torrefied biomass decreased from 0.494 and 1.385 (for TCR-503), respectively, to 0.283 and 0.886 (for TCR-623), respectively. In contrast to its environmental and energy benefits, oxidizable element (i.e., nitrogen) in the torrefied biomass could be released to the atmosphere as nitrogen oxides (NO_x) during combustion. In this regard, the content of nitrogen in the torrefied biomass is relatively high (about 3 wt%) in comparison with most of coals having nitrogen contents below 2 wt% [21].

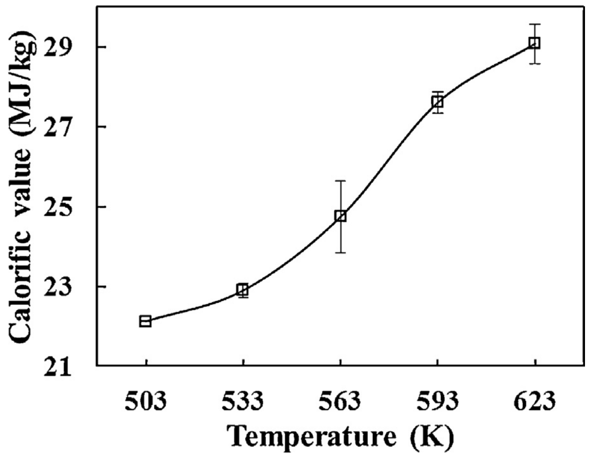


Fig. 4. Calorific value of torrefied biomass as a function of process temperature.

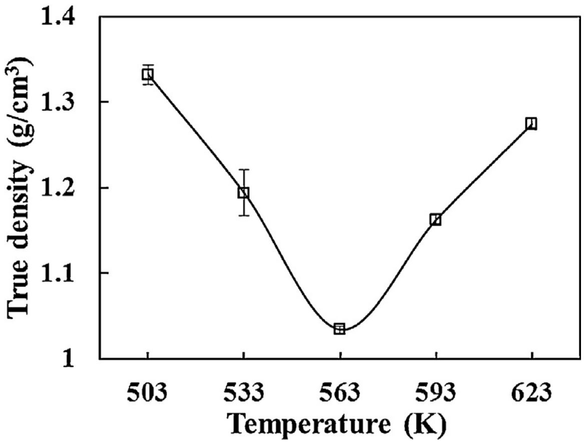


Fig. 5. Helium-based solid density (true density) of torrefied biomass as a function of process temperature.

Some of physical properties of torrefied biomass will affect its behaviors in the thermochemical processes such as pyrolysis and gasification. For example, the pores in a torrefied biomass could increase the potential for lignocellulosic cracking to produce char due to the increase in the residence time of pyrolysis gases in the reaction zone. As a result, torrefaction process can reduce the anisotropic behavior and further impact on the permeability of a torrefied biomass. In this work, the values of the true densities (i.e., 1.332, 1.194, 1.034, 1.162, and 1.274 g/cm^3, respectively) for the resulting products torrefied at 503, 533, 563, 593 and 623 K, respectively, depicted a V-shape variation (Fig. 5). More significantly, this property proportionally increased with temperature. As supported by the SEM pictures in Fig. 6, it showed great differences between these torrefied samples. The resulting products torrefied at the temperature of ranging from 563 to 623 K seemed to be more easily obtained in the structural shrinkage, making it more friable or brittle. As also anticipated from the regular size and arrangement of coffee plant cells, the obvious macroporous structure present in the torrefied biomass can be seen in Fig. 6. However, a decrease in true density may be accompanied by an increase in intra-particle (trapped) pores in the cell wall, which should be stemmed from the thermal devolatilization of carbohydrate components (especially for hemicellulose) between 503 and 563 K, resulting in some light (volatile) gases released and loose structure remained. It should be noted that the contribution to the sample volume of intra-particle pores would be included into the actual measurement of true density because the probe molecule (i.e., helium) cannot penetrate into the trapped pores in the torrefied sample. By

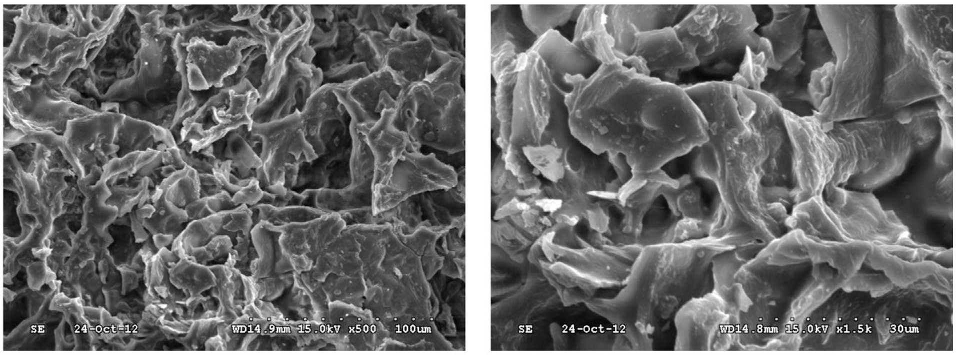
Table 1
Ultimate analyses of torrefied coffee residues (TCR) prepared at temperature range (503–623 K).

Ultimate analysis[a]	TCR-503	TCR-533	TCR-563	TCR-593	TCR-623
Carbon (wt%)	55.10 ± 0.03[b]	56.63 ± 0.04	58.82 ± 0.03	66.77 ± 0.30	67.03 ± 0.30
Hydrogen (wt%)	6.36 ± 0.01	6.22 ± 0.11	6.01 ± 0.01	5.46 ± 0.10	4.95 ± 0.10
Nitrogen (wt%)	2.25 ± 0.03	2.45 ± 0.01	2.64 ± 0.03	3.04 ± 0.13	2.74 ± 0.13
Sulfur (wt%)	Nil	Nil	Nil	Nil	Nil
Oxygen (wt%)	36.29[c]	34.70	32.53	24.73	25.28

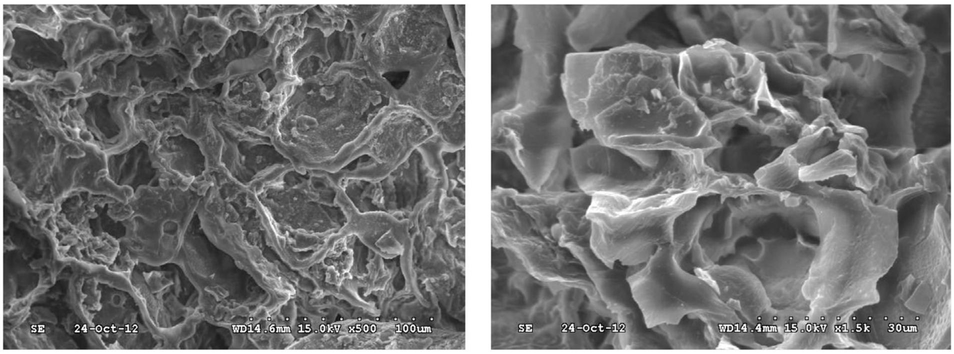
[a] Dry basis.
[b] Average ± standard deviation (for two measurements).
[c] By difference.

contrast, the significant loss of volatile and condensable compounds from the unorganized phase of the torrefied biomass leads to the increase in true density beyond 563 K, leading to the shrinkages of torrefied matrices to form highly carbonaceous materials. Furthermore, the devolatilization may collapse the void volume in the torrefied biomass to raise the true density. Thus, its true density decreased with temperature at above 563 K. This reverse trend can be also attributed to an altered and rearranged polysugar structures. In the present study, the maximum true density was found to be around 1.33 g/cm^3, which is lower that (i.e., about 1.53 g/cm^3) for the wood cell wall [9]. As suggested by Brown et al. [22], the true density may serve as an approximate indicator for pyrolysis temperature used, regardless of the exact thermal history such as heating rate.

(a) TCR-503


SE 24-Oct-12 WD14.9mm 15.0kV x500 100um
SE 24-Oct-12 WD14.8mm 15.0kV x1.5k 30um

(b) TCR-563


SE 24-Oct-12 WD14.6mm 15.0kV x500 100um
SE 24-Oct-12 WD14.4mm 15.0kV x1.5k 30um

(c) TCR-623

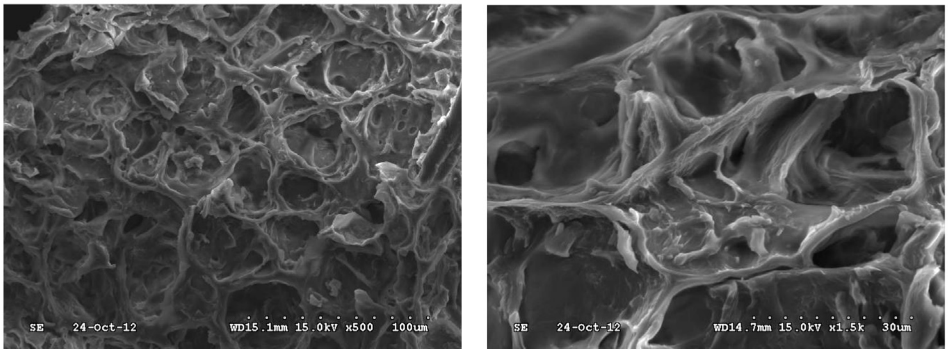

SE 24-Oct-12 WD15.1mm 15.0kV x500 100um
SE 24-Oct-12 WD14.7mm 15.0kV x1.5k 30um

Fig. 6. SEM images (left side: 500×; right side: 1500×) of torrefied products for (a) TCR-503, (b) TCR-563 and (c) TCR-623.

4. Conclusions

The reuse of the coffee residue as energy source has received much attention in recent years due to the economic consideration, energy crisis and environmental issue. However, this biomass often faces several problems, including high moisture content, low heating value and energy density, hygroscopic nature, and smoke during combustion. In this work, the fuel properties of torrefied coffee residue, which was carried out at low temperature (503–623 K) by a commercial electric oven, were investigated by means of calorific value, elemental analysis, true density and scanning electron microscopy (SEM). The results showed that the maximal increase in the calorific value of torrefied biomass occurred at about 563 K, which was in high agreement with the results from the thermogravimetric analysis (TGA). In addition, the carbon content of torrefied biomass increased mostly within the temperature ranging from 563 to 593 K, which should be the temperature window of torrefaction for coffee residue. On the other hand, the torrefied biomass was characterized using helium-based solid density (true density), showing that the density increased with increasing temperature from 563 to 623 K, but decreased with temperature from 503 to 563 K. As observed by the SEM, the torrefied product prepared at higher temperature seemed to be more significant in the structural shrinkage, making it more friable or brittle. This featured change should be caused by the depolymerization of hemicellulose. Therefore, the torrefied coffee residue has greatly improved its thermochemical properties at the optimal temperature (around 563 K), revealing that it can be co-fired with coal in the power plant.

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